THE ORIGIN OF THE NITRATES IN GRIQUALAND WEST.

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The occurrence of nitrate of potash in South Africa has been known for many years, as the farmers in some districts are in the habit of preparing it for their own use from materials occurring in the mountains. Samples of such crystallized saltpetre were received from time to time from the districts of Calvinia, Victoria West, Prieska, Marico, Griquatown, Cradock, and others, but they remained samples only in spite of an eager demand for more.

In the year 1893, considerable excitement was created by the report that extensive deposits of nitrates had been discovered in the Doornbergen, near Prieska, and in the Asbestos Mountains on the other side of the Orange River.

At the request of the Colonial Government, I visited the farm Doornbergfontein, at the south-eastern extremity of the Doornbergen, and subsequently a large number of farms between Prieska and Griquatown on behalf of private enterprise. During my visits to these regions, I had ample time to study the question of the origin of the nitrates, and as the results of my observations and subsequent experiments appear to me to be of some interest, I venture to lay them before you to-night.

The Doornbergen and the Asbestos Mountains form one range of low hills extending from the north of Griquatown to the south-west of Prieska, and are separated from each other by the valley of the Orange River. The slates and quartzites of probably Devonian age, of which they consist, are highly ferruginous, and often so finely laminated that, on exposure to the action of atmosphere, they cleave into large sheets, as thin as window-glass, or even writing-paper. Other portions are more solid and compact, and if pieces are struck against each other they ring like glass, owing to the large amount of silicates of iron and lime which they contain.

A peculiar feature of these hills is that the numerous valleys and gorges which traverse them, and branch out in all directions, are lined on both sides by perpendicular or overhanging cliffs, one hundred or more feet high. These cliffs are often so continuous on all sides that farmers are able to convert such valleys into camps for their horses or cattle, by putting fences across the entrances.

It is along the base and in the caves of these overhanging cliffs that the nitrates and the nitrate-bearing materials occur. The nitrates fill the fissures of the laminated rock, and incrustate their surface as finely crystallized nitrate of potash, while the soil and débris under the cliffs contain a variable amount of saltpetre, which often forms lumps more or less pure, or cements the débris of the rock into lumps and blocks of considerable size. The richest material is always at the base of the cliff, but only in those places where the rock is finely laminated, and the overhanging parts protect the foot of the cliff against rain.

Throughout the whole region which I investigated, and in which I spent more than three weeks, I found the source of these nitrates to be the refuse and the remains of animals, principally the fæces of the rock rabbits (*Hyrax Capensis*). In every single case where the nitrates were not accompanied by such remains, I was able to trace their origin to caves or crevices in the rocks above containing such materials. That similar animal remains are the source of nitrates in most other countries where they occur has been known for a long time, and it has been shown recently that the nitrification of the ammonia evolved by them is due to the action of microbes.

A. Müntz and V. Marcano* have proved that the saltpetre-earth which occurs in the vast caves of the Andes in South America (not to be confounded with the nitrate-fields of Tarapaca in Chili) is being formed in this way from the guano of birds and bats, and that of the caves of Venezuela from bones and fossils. Their attempts to isolate this microbe in the usual way failed, because, as was found out later on, it did not grow on gelatine or similar mediums.

A year later, however, Winogradsky† succeeded in isolating a nitrifying bacillus from soil near Zurich, by a very ingenious and tedious method, and he named it *Nitromonas*, on account of its peculiar shape.

In 1894 Dr. Tolomei,‡ professor at the military academy at Florence, published the results of his investigations into the cause of the formation of nitre on the walls of some buildings at Florence, and proved conclusively that it was due to the action of a microbe.

Thinking it very desirable to ascertain whether the nitrification in the cliffs and caves of the Asbestos Mountains was due to a similar cause, I provided myself with sterilized tubes, filled them with samples

* A. Müntz and V. Marcano, 'Comptes Rendus,' 1889, p. 900.

† S. Winogradsky, 'Annales de l'Institut Pasteur,' 1890, Nos. IV. and V.

‡ G. Tolomei, 'Contribuzione allo Studio del Fermento della Nitrificazione, published in *Le Stazioni sperimentali agrarie italiane*, March, 1894, vol. xxvi.

of soil and refuse from several cliffs, and carried out the necessary experiments after my return to town.

A quantity of coarse sea-sand was washed with acids and water, dried, ignited, mixed with 1 per cent. of chalk, and distributed into six porcelain basins. After the basins and their contents had been sterilized, they were placed under separate bell-jars, together with a little basin of sterilized water, in order to provide the necessary moisture. Three of them were devoted to series A, and three to series B, of the experiment.

In series A each basin received 5 ccm. of a solution of sulphate of ammonia,* just enough to moisten the sand. The first basin received nothing else; to the second was added 1 ccm. of a decoction of a little soil from one of the caves; and to the third one ccm. of a liquid obtained by shaking a sample of such soil with some sterilized water.

In series B the first and third basins received 5 ccm. of a decoction of fæces of rock rabbits, and the second one a liquid obtained from the same material by cold maceration only. The first received nothing else, but the third basin an addition of a few drops of the liquid used for the second dish.

I need hardly add that all instruments used for these operations had been sterilized beforehand, and that each experiment was made in duplicate. The six bell-jars were placed in a room with closed shutters, and kept for twenty days.

On analyzing the contents of the six basins, I found the following results:

Series A.

1. No trace of nitrate.
2. No trace of nitrate.
3. Nitrate present, corresponding to 0·0008 nitrogen.

Series B.

4. No increase of nitrate.
5. Considerable increase of nitrate, corresponding to 0·0015 nitrogen from 0·0003.
6. Same as No. 5.

These results show that no nitrate was formed in the sterilized materials, but that it was formed in the unsterilized animal matter, and in the basins to which a little fresh substance had been added.

In order to ascertain the presence or absence of microbes in the different samples of sand by direct observation, I took a little of each, shook it with sterilized water, mixed 1 ccm. of each sample of water

* Ammonium sulphate and potassium sulphate each one gramme dissolved in one litre of distilled water and sterilized.

with sterilized gelatine, and kept the gelatine plates in the usual way for two days.

On plates Nos. 1, 2, and 4, not a single colony of microbes appeared; on plate 3 their number was considerable, *viz.*, 27,000 per ccm. of sand, and on plates 5 and 6 much larger, *viz.*, 118,000 and 60,000 respectively.

These results coincide well with those of the chemical analysis, and prove that the nitrification of these materials is a process quite similar to that in other countries.

Having ascertained by local observations and subsequent experiments that the nitric acid of these nitrates and nitrate soils is derived from the accumulated refuse and remains of animals, specially of the rock rabbits, it will be necessary to show whence the other ingredient of the saltpetre, *viz.*, the potash, is derived, and how the pure substance could have accumulated in such considerable quantities as one finds it.

The potash is probably derived from the rock as well as from the fæces. A sample of rock which I analyzed had the following composition:

Silica	35·3	Magnesia	·03
Ferric oxide	55·66	Potash	1·72
Alumina	5·38	Soda	·61
Lime	1·15	Moisture	·13

Of special importance for the process of nitrification is the presence of lime in the rock, for Professor Tolomei's experiments have shown that the nitrifying microbes grow only in the presence of a basic substance like lime or magnesia. He has also demonstrated that porous material favours the nitrification considerably.

Both these conditions are well fulfilled in our case. The finely laminated shales become impregnated with the compounds of ammonia contained in the drainage from the animal remains, and in the fumes formed during their putrefaction. The fine fissures between the layers act like the pores in the soil, and the ammonia is well exposed to the action of the nitrifying agents.

The result is the formation of the nitrates of potash and lime, of which the latter is very hygroscopic, and attracts moisture from the atmosphere whenever the air becomes damp. One day I could hardly notice any saltpetre along a cliff which I had seen glistening with white efflorescence the day before, although it had not rained as yet. The moisture of the atmosphere had been sufficient to dissolve the film of nitrates on the surface of the rocks. This solution of nitrates spreads and descends along the shales, and the saltpetre crystallizes again when the moisture evaporates. Being thus repeatedly dissolved and recrystallized, it becomes purer and purer, and being a very soluble salt, it creeps by efflorescence to the projecting points of the rocks, and accumulates in the soil and on the rock at the base of the cliff. The nitrate of calcium, however, being more soluble in water than the nitrate of potash, would not be separated from it by this natural refining. That is done by a secondary chemical action.

In all the samples of nitrate-bearing soil* which I analyzed, I found a considerable amount of sulphate of lime; and in a few localities tooth-like pieces of saltpetre and gypsum occurred close together on the rock just near the surface of the soil. The peculiar form of these specimens proves that both were formed very slowly on the spot by the double decomposition of nitrate of calcium and sulphate of potassium, the sulphur being derived from the albuminoids of the refuse matter.

Most samples of apparently pure saltpetre, even if free from mechanical impurities like clay or sand, still contain nitrate of lime, and traces of sulphate of lime and chloride of sodium; but a few colourless transparent specimens which I found are chemically pure nitrate of potassium.

From the preceding description, it is apparent that the occurrence of saltpetre in this region has no resemblance whatever to the nitrate-beds of South America, where the saline material (chiefly nitrate of soda) forms layers many feet thick, and spreads over hundreds of square miles. Nor is it like the deposits in North America, Venezuela, and several other tropical countries, where the remains of antediluvian animals, accumulated in caves in layers ten to thirty feet deep, have undergone nitrification and formed nitrate soils, which principally contain the nitrates of potassium, calcium, and magnesium.

To a certain extent it may be compared with some localities in India and Ceylon, where the walls of caves filled with bat guano gradually become incrustated with nitre.

A much more exact comparison, however, is offered by the artificial manufacturing of saltpetre as it was formerly carried out in Southern Europe. In the so-called saltpetre-gardens animal refuse and waste-products were spread over soil mixed with lime, and thus exposed to the nitrifying agents. The first product of this operation was nitrate of calcium, which was decomposed into nitrate of potassium by the addition of pearlash—processes almost identical with those described above.

But this natural chemical factory not only produces the crude

* Composition of a sample of nitrate-soil:

Potassic nitrate	25·23	Organic matter	15·76
Calcic nitrate	4·28	Insoluble in water after ignition (oxide of iron, clay, sand)	34·11
Magnesic nitrate	1·14	Moisture	11·39
Calcic sulphate	4·86	Not determined	2·18
Sodic chloride	1·12		

substance: it purifies and refines it also by recrystallization, until it sometimes produces an article as pure as any made by a chemist.

It may appear somewhat strange that the little rock rabbit should have been capable of supplying the raw material for such quantities of nitrates and nitrate-bearing soil as occur in these mountains.

The conditions for the formation of nitrates exist in almost all our mountains, not excepting those of the Peninsula. In caves that are inhabited by rock rabbits, the nitrification of their refuse is proceeding, especially in summer, on Table Mountain as well as in the Karroo and on the banks of the Orange River. But the nitrates cannot accumulate here, because every winter washes away what was formed during the summer. Hence, it is not surprising that samples of such soil from Table Mountain usually do not contain more than ½ per cent. of nitrates of calcium and potassium.

In those dry regions, however, the climate allows the accumulation of the fæces of the rock rabbits from year to year, from century to century, from thousands to thousands of years, just as it favoured the preservation of the guano on the islands along our western coast. And all this time the nitrification, the lixiviation, the crystallization and recrystallization, went on, until cliffs hundreds of yards long were saturated with nitrates, and thousands of tons of nitrate-bearing débris had accumulated under their shelter.

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